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CHEMICAL DYNAMICS

Essai de Mécanique Chimique fondée sur la Thermochemie. Par M. Berthelot. Two Vols. (Paris : Dunod, Editeur, 1879.)

THE problems which the chemist attempts to solve may be broadly divided into two groups. In studying the heterogeneous distribution of molecules, the chemist finds that new relations of molecules, in other words, new substances, are produced; he must study the composition and properties of these substances. He also finds that these changes involve a consideration of the relative positions of the changing body and of other bodies, that is to say, he recognises the action of force. He must endeavour to determine the laws of action of this force. The study of the properties and composition of substances has received more attention than that of the general laws of chemical force; both methods of investigation must, however, be applied to chemical phenomena, before these can be fully explained.

The general properties of a compound may be regarded as depending chiefly on the composition of that compound, or chiefly on the function or "power of doing" of the compound. There have always been schools of chemistry which paid most attention to composition, as there have been schools which made function pre-eminent. Modern chemistry is attempting to connect both in a general scheme of classification; whilst at the same time she endeavours to learn the conditions under which chemical force is exerted, and hopes thus to elucidate general laws.

The atomic theory, which is one great outcome of the study of the composition and function of chemical substances, has of late years been merged in the wider molecular theory of matter.

This theory, assuming the existence of a grained structure in matter, proceeds to deduce, by dynamical reasoning, the amount of motion existing among these little parts of which matter is built up. The laws of Boyle and Charles are among the primary results of this deduction. But under certain conditions gases do not exactly obey these laws; hence the theory asserts that under certain conditions the molecules exert mutual action.

Another deduction from the theory is the statement usually known as Avogadro's law—"Equal volumes of gases at the same temperature and pressure contain equal numbers of molecules." This statement provides the chemist with a means for determining molecular weights. But the chemist in applying Avogadro's law is obliged to admit that in many reactions the parts of molecules really part company. He attempts to picture to himself this molecular splitting.

Let the molecule A consist of two parts, a and b, the molecule B of two parts, c and d; let these parts be in motion. Under certain conditions the stress between a and c and the stress between b and d may be greater than that between a and b, and c and d; the original molecules are decomposed, and new molecules, C and D, are formed. The stress between a and c considered from the point of view of a or c alone is a force exerted by a on c or by c on a. This force is the force of chemical affinity.

The result of the action of this force is a new configuration of the system A B; the energy of the new system, C D, will be different from that of the original system.

Chemical action, thus regarded, is a re-arrangement of parts of molecules under the influence of the force called affinity. Chemical energy is thus regarded as potential energy.

Now a chemical action between A and B will take place under certain definite conditions only, hence although the absolute value of the affinity of A for B may be a constant, the course of the change and the entire result of the change will nevertheless be largely dependent on physical conditions. No force may be exerted except at high temperatures; the change of momentum of A will depend on its position relative to B; the relative positions at which this change occurs may only be gained at high temperatures. The force exerted may be small; still if a chemical change occur at all, there must be an action between the parts of A and the parts of B.

Now let this mutual action begin, let no energy be added to the system from without, but let the system as a whole lose energy; the energy so lost may be measured in the form of heat. But more than one re-arrangement of the parts of two molecules may frequently be possible; which will be produced? A system is in equilibrium when its entropy (using the term in the Clausian sense) has reached a maximum. Hence that system whose entropy is the greatest of the entropies of the possible systems will be produced.

This is substantially Berthelot's "law of maximum work," a law which lies at the foundation of his system of thermal chemistry. But a system not marked by possessing the largest amount of entropy of all the possible systems, may nevertheless be the most stable under the experimental conditions; the stability will depend on pressure, temperature, relative masses, &c. Hence in order to determine the actual result of a chemical action, the conditions of stability, in other words, the relations to temperature, pressure, &c., of the various possible products of the reaction must be known. The necessity of this knowledge is insisted on by Berthelot. To determine, therefore, the product of a given chemical action one must measure the quantities of heat evolved in the passage of the system from the standard state to each of the possible new states, and one must know the conditions of existence and stability of each of these states This problem therefore presents both a chemical and a physical question for solution. The solution of the chemical question is much aided by a knowledge of the laws of atom-linking; but these cannot be here considered.

A measurement of the heat evolved in a chemical change evidently enables us to find the difference between the energy of the original and final chemical systems; the total heat change being independent of intermediate states through which the system may pass. So if work is done on a chemical system whereby it is caused to assume a new configuration, this work measures the energy transferred from the initial to the final system; in this case heat will be absorbed during the chemical change.

But in actual chemical reactions the action of the chemical force proper will be interfered with and complicated by physical, or secondary forces. So much is this the case, that for many years these actions were not distinguished.

One school simply measured the quantity of a substance A, which was needed to act on B to produce C; the greater the quantity of A required to act on a given weight of B, the greater was the affinity of A for B. With this school all was chemical. With Berthollet, on the contrary, all was physical; but facts have been discovered since the publication of the "Statique Chimique" which have necessitated a reconsideration of his laws.

Gradually the meaning of affinity has been made clear. The greatest contribution towards this end is undoubtedly the papers of Guldberg and Waage, whose work has been sketched by the present writer in this journal (vol. xx. p. 530). The Swedish naturalists disregard the action of secondary forces in their method of determining the ratios between the affinity coefficients of various substances.

The importance of a measurement of the change of energy accompanying the passage of a chemical system from one specified state to another; the importance, in other words, of a measurement of the heat evolved or absorbed in such a passage, is at once apparent. But this measurement—even taken along with a general knowledge of the conditions of existence of the various possible systems—does not enable us certainly to predict the result of the chemical action. If we had a complete knowledge of the mode of variation of the potential energy of a system with changes in the configuration of the system, then it *might* be possible for mathematicians to predict all possible arrangements of the system under the action of specified external forces. But having made heat measurements only, we are very far indeed from this point.

Indeed the fundamental assumption that chemical energy is wholly potential, and depends on the arrangement of the parts of a system, may be false; and even if this assumption be true we know nothing as yet of the relation between this energy and the configuration of the system.

The heat absorbed or evolved in a chemical change measures the total work done by the system in its passage from one specified state to another, but it is evident that it does not directly measure the true force of affinity. The stress between the parts of two molecules may be small, yet under certain conditions a chemical change may occur; the loss of energy in the formation of the new system may be considerable, and hence the heat evolved, considerable. Chemical affinity thus regarded is a kind of liberating force.

For the measurement of the ratios of the affinities of various systems, Guldberg and Waage's method is to be preferred to the thermal method of Berthelot. For a full consideration of chemical equilibrium Berthelot's method is altogether insufficient, although it has *largely* advanced the solution of this problem.

The method of Willard Gibbs seems the only feasible one in the present state of the chemical and mathematical sciences. In this method (see NATURE, vol. xxi. p. 516) the energy and entropy of a system are considered—the stability of a system depends on the component masses, volume, and entropy (the *magnitudes* of the system); and on the temperature, pressure, and *potential* (the *intensities* of the system).

The stability of a system is chiefly dependent, according to Berthelot, on the amount of heat evolved in the passage to the given state from an initial state, and on the general properties of the given system as compared with other possible systems. This is evidently a much cruder statement than that of Gibbs. Berthelot's principle of maximum work is indeed one among many deductions made by the method of the American professor.

Both methods lead to a recognition of chemical equilibrium as an outcome of chemical action; the conditions of the latter are considered before those of the former; chemical kinetics precedes chemical statics. The usual method of the text-books is to make chemical equilibrium all-important, and barely to mention the subject of chemical kinetics.

It is evident that the time when it will be possible to treat chemical problems by a purely dynamical method is yet distant. The method of Gibbs leads the way in bringing chemical generalisations under the domain of the principles of energy, and it does this without assumptions about the action of the parts of molecules; the method is a thermo-dynamical one.

Berthelot's method, on the other hand, is thermo-chemical; but a thermo-chemical method seems to promise the largest development in the present state of the science.

Berthelot perhaps claims too much for his method: in his great work he is not always definite in his use of such terms as "force," "affinity," "energy," "work;" nevertheless the "Essai de Mécanique chimique" is undoubtedly a great work. To Berthelot (and to Thomsen) is due the honour of having steadily pursued the thermo-chemical method for many years, and of having collected masses of most important facts; and he has now enriched chemical science by the publication of these results in a collected and systematic form, in a treatise full of original ideas and suggestive of almost unlimited topics for future work and discussion. What a field of work is opened before one in this book! To determine that this body is produced by the action of these bodies is not enough; indeed it is scarce a beginning. Chemical science has higher aims. The changes of energy which accompany changes of configuration of matter must be measured; the physical and chemical constants of all the products of a chemical change must be determined with care, the velocity of the change must be measured, and an attempt must be made to apply dynamical reasoning to the results thus obtained.

The first volume of the "Essai," entitled "Calorimétrie," begins with general remarks on thermo-chemical work, and on affinity; after laying down certain general theorems concerning chemical reactions, and illustrating the application of these in the formation of insoluble and soluble salts, the formation of series of carbon compounds, &c., a detailed account is given of experimental calorimetric methods; this is accompanied by numerous tables of specific heats, heats of combination, heats of solution, heats of formation of salts in solution, heats accompanying isomeric changes, &c. The second volume—entitled "Mécanique"—is concerned with a study of the conditions which determine chemical changes. This general study divides itself into two branches: chemical decompositions and recompositions—included under the title of "Dynamique Chimique"; and secondly those final distributions of matter which result from reciprocal actions between simple or compound bodies, grouped together as "Statique Chimique." Would it not have been better to have entitled the general subject "Chemical Dynamics," and the branches "Chemical Kinetics" and "Chemical Statics" respectively?

It would obviously be impossible to give here even an outline of Berthelot's treatment of this immense field of work; one or two instances must suffice.

The two fundamental generalisations of the French chemist have already been mentioned. Let us turn to his treatment of the specific heats of elementary bodies and of chemical equilibrium.

Berthelot refuses to accept the law of Dulong and Petit as applied to solid elements. He says that the actually-determined specific heats of the elements vary much with temperature, and that the products of these numbers into so-called atomic weights are of very different values. He gives a list of 11 elements, the specific heats of whose *equivalents* is about 6·4; and a list of 31 for which the product of specific heat into equivalent weight is about 3·2.

This result well illustrates what will probably be regarded by most chemists as a fundamental error on the part of the author of the "Essai"; Berthelot is still to be classed among the staunch supporters of the system of notation founded on equivalents. In this country we have no such phenomenon as a great chemist who writes the formula of nitric acid AzO_5. Nevertheless Berthelot's thermal chemistry is founded on a molecular theory. He constantly speaks of molecules and of action between the parts of molecules; he also speaks of the architecture of atoms, and seems to regard the modern atomic theory as utterly opposed to such an idea.

> "The kinetic energy of the molecule may be regarded as made up of two parts—that of the mass of the molecule supposed to be concentrated at its centre of mass, and that of the motions of the parts relative to the centre of mass. The first part is called the energy of translation, the second that of rotation and vibration. The sum of these is the whole energy of motion of the molecule. The pressure of the gas depends on the energy of translation alone. The specific heat depends on the rate at which the whole energy, kinetic and potential, increases as the temperature rises." (Clerk Maxwell, *Chem. Soc. Journ.*, 13, 502.)

In the present state of our knowledge of the internal motion of the parts of a molecule it is impossible to determine satisfactorily the ratio of the two parts of the energy of the molecule, and it is extremely difficult to reconcile the observed with the calculated ratios of specific heats.

Nevertheless, if we adopt the mean numbers found for the specific heats of the solid elements and multiply these into the maximum atomic weights as determined by the aid of Avogadro's law, we get a result which is too constant to be merely accidental. Taking Kopp's numbers, calculated from specific heats of compounds, for those elements which have not yet been obtained in the solid form, we find that the product of specific heat into atomic weight (*not equivalent weight*) is about 6·4 for forty-four elements, about 5·5 for ten elements, less than 5 for two elements, and is yet unknown for eight elements. Furthermore we find that the specific heats of the elements are fairly constant, provided they be determined for a temperature-interval known to be considerably below the temperature of fusion of the elements.

We seem, therefore, fully justified in accepting the law of Dulong and Petit as an empirical statement of very considerable value, although not as a final statement of the connection subsisting between the ratio of the two parts of the energy of the elementary molecules, and the relative weights of the parts of the same molecules.

In treating the subject of chemical equilibrium Berthelot first of all examines processes of chemical combinations in general, and contrasts these with processes of decomposition; he then studies those changes which are made up of two parts—a direct and reverse—and which are characterised by the attainment of a limit dependent on conditions of temperature, pressure, relative masses, &c. The chemical equilibrium thus established he divides into two kinds: equilibrium of homogeneous bodies, *i.e.*, when the original and final substances are all liquid or gaseous and capable of complete admixture during the course of the change; and equilibrium of heterogeneous bodies, *i.e.*, when some of the substances are solid and some liquid, or some liquid and some gaseous, or when all are liquid or gaseous, but are nevertheless incapable of complete admixture. Examples are given of each kind of equilibrium, and of the conditioning influence of temperature, pressure, mass of solvent, contact with other substances, relative masses of reacting bodies, chemical functions of reacting bodies, velocity of the change, &c. The phenomena of equilibrium of heterogeneous systems lead to a discussion of dissociation; this to a consideration of precipitation, and thence to an instructive chapter on the state of salts in solution, and the meaning of the terms "feeble" and "strong" as applied to acids and bases.

Although, in considering Berthelot's treatment of chemical equilibrium, one misses the bold and fascinating results obtained by Gibbs in his great paper on the "Equilibrium of Heterogeneous Substances," and the exactitude and simplicity of the beautiful theory of Guldberg and Waage, and although one cannot but much regret that he should not have written his formulæ and equations in a language more easily understood by the chemist of to-day, one must nevertheless admire the breadth of view, the felicity of illustration, and the suggestiveness of the work of the French chemist.

The publication of the "Essai" marks an important point in the advance of modern chemistry: it comes to the chemist with the message, amongst others, that his science demands more than the stereotyped so-called original investigation, in which are detailed a few properties of a number of new compounds produced by methods long ago marked out and defined; it tells him that he must revise and advance his methods, that he must try to explain his facts by appeal to principles, that he must not be afraid to strike off the beaten path into the by-ways of research, and that there is more to be hoped for in a bold impatience than in the "Smooth diffused tranquillity of heartless pains."

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A JAPANESE ROMANCE

Chiushingura, or the Loyal League; a Japanese Romance. Translated by F. V. Dickins, B.Sc., of the Middle Temple, Barrister-at-Law. (London: Allen and Co., 1880.)

THIS book is one of great value and interest, both from a purely literary and from an anthropological point of view, and further as yielding a most instructive lesson in the meaning of Japanese pictorial art. Mr. Dickins is well qualified for the task which he has performed, being not only a practised Japanese and Chinese scholar, but a man of very wide attainments in various branches of natural science, and he has been able to supply a series of most valuable explanatory notes in the appendix of his work. It may be mentioned that he commenced his career by graduating in science and medicine at the University of London, and that after having served for some years as a surgeon in the navy he was called to the bar, and practised his profession for many years at Yokohama, where, by constant study, he became deeply versed in all that pertains to Japanese life and customs.

The present work is illustrated by the actual Japanese woodcuts with which the Japanese edition of the historical novel of which it is a translation is embellished. The woodcuts were printed in Japan by native workmen, and are now bound up with the English text. The reader is therefore able to form an exact conception of the ideas which the Japanese artist has intended to convey in the twenty-nine pictures which the work contains. It is most interesting to all who are in any way attracted by Japanese art to realise the mode in which the emotions, such as rage and despair, laughter and pain, are depicted, and to join as it were in a Japanese game of blind-man's-buff. The "Chiushingura, or Loyal League," is an historical romance which embodies the history of the forty-seven Ronin so well known from Mr. Mitford's account of it in his fascinating "Tales of Old Japan." The present romance is one of the most popular and best known in Japan, or rather was so, for its main object is to glorify "Chiushin," or loyal-heartedness, the supreme virtue of the Bushi class under the old order of things that passed away with the year 1868. Disloyalty was considered to be the meanest of crimes, rendering the person guilty of it unworthy of existence, and the Japanese self-despatch, seppuku, which occurs abundantly in the romance, was a self-inflicted atonement for this crime, and in no sense a mere ignoble suicide.

The action of the romance is laid in the fourteenth century, although the events on which it is founded really occurred at the beginning of the eighteenth, the author having been compelled to disguise barely the reality by diluting the history with a certain amount of fiction, and altering names and dates so as to evade the law which, under the Shogunate, attached severe penalties to the publication of recent or current events of a public character.

We cannot detail the plot of the story, but will give a few extracts. A highway robber after murdering an old man soliloquises thus as he kicks the body aside: "Wretched piece of work. Well, I am sorry for it. I did not do it out of any malice, but you see you had money, that killed you. No money, and you'd be alive now. Your money was your enemy. I can't help pitying you. Which prayer are you for? Namu amida butsu, or Namu miyôhô renge-kiyô? Choose one, and let all end." The prayers are Buddhist, the words being Sanskrit ones which have undergone much Japanese alteration.

The story closes with the account of the attack of the forty-seven Ronin on the castle of Maronhao, the murderer of their lord Yenya (by "murderers" being meant the persons who compelled Yenya to perform seppuku). Their mode of proceeding is very quaint. In the very heat of the attack, just as they burst into the dwelling of their victim, the leader of the expedition, in true style of a Japanese general, calmly seats himself on a camp-stool and gives his orders. The neighbours on either side are roused by the noise and send their retainers to see what is going on. "Ya ya," they cry, "what means all this uproar and confusion, clashing of weapons and hurtling of arrows? Are you attacked by rioters or by robbers, or has a fire broken out somewhere? We have been commanded to find out what is going on, and inform our masters of the cause of disturbance." The Ronin answer, "We are liegemen of Yenya Hanguwan; some forty of us banded together to revenge our lord's death upon his enemy, and are now struggling to get at him. We are not rising against the Government, still less have we any quarrel with your lords. *As to fire, strict orders have been given to be very careful*, and we beg you not to be under any apprehension on that score. We only ask you to leave us alone and not to interfere with us. If as neighbours you should think yourselves bound to assist our enemy, we shall be obliged, despite our inclination, to turn our weapons against you."

To these bold words the retainers of the noblemen shout back approvingly, "Right well done, right well done; in your place we should feel ourselves bound to act as you are acting; pray command our services." So they desert the roofs and put out their lights.

When Maronhao is at last caught he is treated with ceremonious respect, and afforded the opportunity of performing suicide in the usual manner. "We pray you pardon our violence, and beg of you that you will *present us with your head* according to the usage of our country." But Maronhao is a vile, ungentlemanly ruffian, and drawing his sword under pretence of ripping himself up, he makes a treacherous lunge at the leader of the Ronin So he is at once despatched without more ado. The head is cut off with the dagger with which Yenya committed "seppuku," and is struck at in frenzy, gnashed at, and cried over in grief and fury by the Ronin. Then it is washed, and presented on a small stand before the "ihai" (a tablet inscribed with the posthumous name of the deceased) of Yenya placed opposite to it on a similar stand. Incense is burnt before the "ihai," and a prayer is offered up to the dead Yenya "resting amid the shadows of the tall grass" (in the grave), that he will look with favour on the offering. Then all the Ronin betake themselves to his grave and perform "seppuku" themselves.